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Robert W. Meulenberg and Jonathan R.I. Lee

Intriguing Physics of Quantum Dots

The study of nanometer sized semiconductor crystallites, also known as quantum dots (QDs), has seen rapid advancements in recent years in scientific disciplines ranging from chemistry, physics, biology, materials science, and engineering. QD materials of CdSe, ZnSe, InP, as well as many others, can be prepared in the size range of 1 – 10 nm producing uniform, nearly monodisperse materials that are typically coated with organic molecules [1-3]. The strength of charge carrier confinement, which dictates the size-dependent properties, in these QDs depends on the nature of the material and can be correlated to the Bohr radius for the system of interest. For instance, the Bohr radius for CdSe is ~5 nm, while in the more covalent structure of InP, the Bohr radius approaches ~10 nm.

The study of CdSe QDs has been particularly extensive during the last decade because they exhibit unique and tunable optical properties and are readily synthesized with high-crystallinity and narrow size dispersions. Although the core electronic properties of CdSe are explained in terms of the quantum confinement model [4], experimental efforts to elucidate the surface structure of these materials have been limited. Typically, colloidal CdSe QDs are coated with an organic surfactant, which typically consists of an organo-phosphine, -thiol, or -amine, that has the function of energetically relaxing defect states via coordination to partially coordinated surface atoms. The organic surfactant also acts to enhance carrier confinement and prevent agglomeration of the particles. Chemically, it has been shown that the bonding of the surfactant to the CdSe QD occurs through Cd atoms resulting cleavage of the Se atoms and formation of a Cd-rich (i.e. non-stoichiometric) particle [5].

Magnetism in Doped Quantum Dots

Methods for the synthesis of magnetic QDs via chemical doping has gained significant attention in the last few years due to their potential usage in magnetic applications such as spintronics, magnetic switching, and magnetic recording (see Ref. 6 for a recent review). The primary challenges with doping QDs include controlling dopant location, concentration, and oxidation state as these can affect the electronic, optical, magnetic, and structural properties of the QD. Although the first report of Mn^{2+} doping in a QD material using a room temperature synthesis method was achieved as early as 1994, it was not until 2000 that successful Mn^{2+} doping in colloidal CdSe was reported. Low doping efficiencies were attributed to a "self-purification" mechanism that rendered CdSe "undopeable", but recent reports have shown that Mn^{2+} doping is possible in CdSe QDs. Although Mn^{2+} doped CdSe QDs exhibit robust optical properties related to the Mn^{2+} guest ion, a potential drawback of chemical doping is that the size-dependent optical properties of the CdSe QD are perturbed. It would be desirable, therefore, to prepare CdSe QDs that retain the native optical properties observed in the undoped material while inducing intriguing magnetic effects. This task can be accomplished by manipulation of the QD surface chemistry, rather than introduction of a chemical dopant.

Inducing Magnetism in Quantum Dots Without Chemical Dopants

The appearance of magnetism in otherwise non-magnetic materials has recently been reported for a number of nanoscale systems. For instance, two previous studies have shown that Au, a $5d^9$ metal, exhibits ferromagnetic behavior in the nanocrystalline form [7] but the authors have proposed conflicting mechanisms. Demonstrating the appearance of magnetism on a system with a closed d-shell, such as Cd or Zn, would be a remarkable result as these materials should exhibit diamagnetic behavior. Recent reports in the literature have observed effects of induced magnetism for CdSe QDs [8], but again, there exists much debate as to the exact mechanism for the observed mechanism. Adding more complexity to these observations is the fact that none of these studies systemically investigate both the size and surface ligand effects and the authors of two of these reports [8b, 8c] claim that the observed magnetism is due to ferromagnetic ordering. As such the magnetism remains the subject of some controversy in the literature
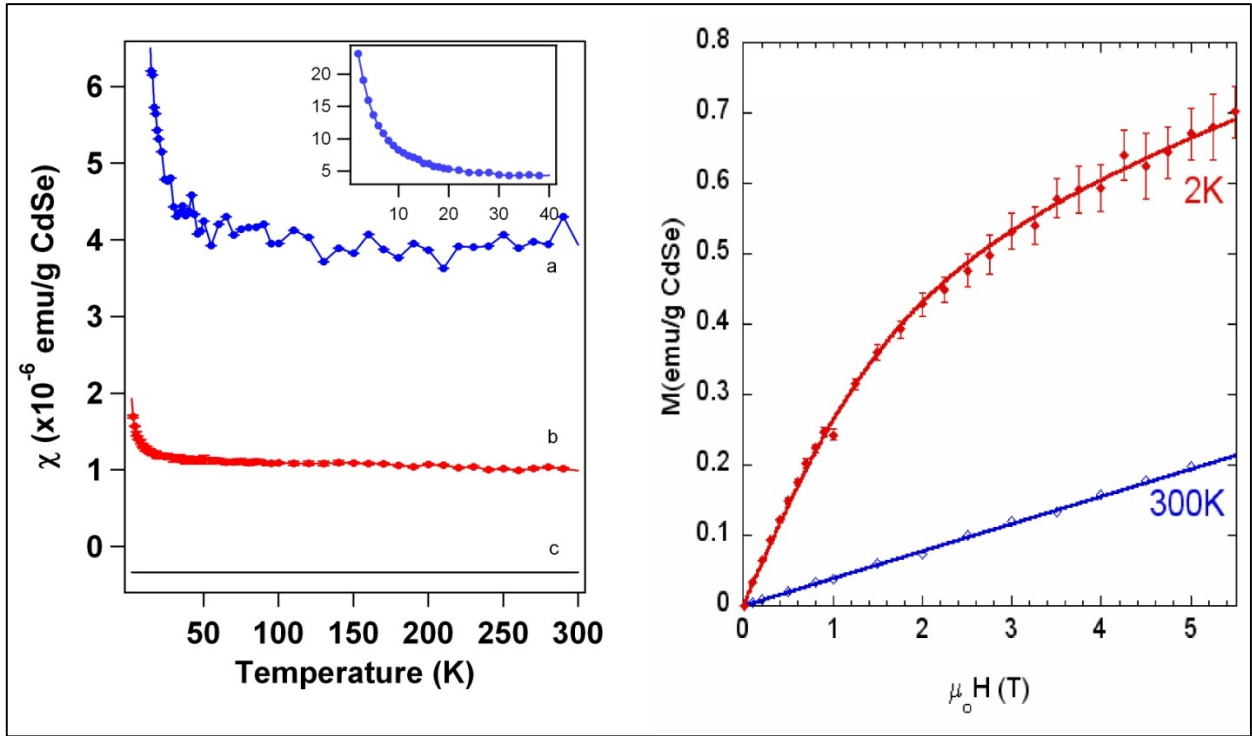
Figure 1. (A) Magnetic susceptibility for 3 nm CdSe QDs passivated with (a) TOPO, (b) HDA, and (c) bulk CdSe. (B) Isothermal magnetization for 2.8 nm CdSe-TOPO QDs at two temperatures. Inset of (A) plots an expanded view of the low temperature susceptibility [ordinate and abscissa same as in (A)]. It should be noted that atomic emission measurements indicate non-Cd transition metal impurities are <1 ppb.

and identifying the origin of the magnetism is an extremely important goal   Our group has been involved with experiments that attempt to help identify the exact nature of induced magnetism in CdSe QDs using both traditional magnetometry and x-ray absorption spectroscopy [9]. In Figure 1, both temperature dependent and isothermal magnetization are shown for ~3.0 nm CdSe QDs. Figure 1A displays the magnetic susceptibility for CdSe QDs passivated with hexadecylamine (HDA) or trioctylphosphine oxide (TOPO) and the expected value for bulk CdSe. Of particular interest are two effects: (1) The appearance of a low temperature Curie tail and 2) the temperature independent part of the magnetic susceptibility (χ) is positive for both QD samples. The Curie tails arise from paramagnetism in the QD samples at low temperatures. The mechanism by which this can occur can be understood by examining the temperature independent part of the magnetic susceptibility. The appearance of positive χ values is intriguing because bulk CdSe and the organic ligands have negative χ indicating that the total χ for the QDs should be slightly more negative than that of bulk CdSe. The appearance of positive χ arises from a Van-Vleck contribution in the form of a charge transfer effect on the QD surface. This charge transfer effect can manifest itself in the form of π-backbonding, with the degree of backbonding depending on the ligand π-acceptor strength. Following the π-acceptor scale, we expect TOPO > HDA as a π-acceptor and similar trends in the strength of charge transfer.
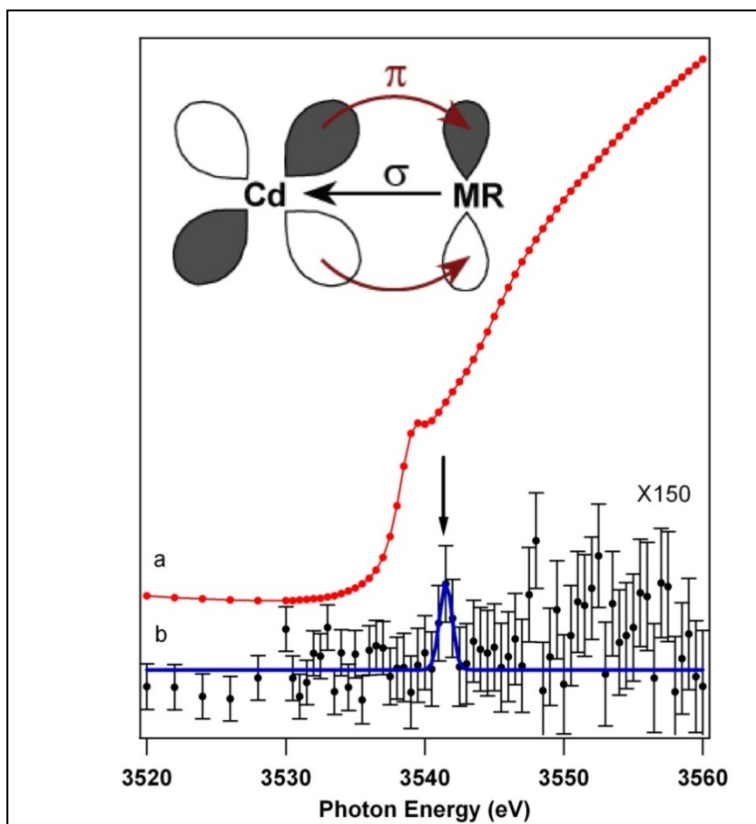
We have also performed x-ray absorption (XAS) and x-ray magnetic circular dichroism (XMCD) measurements at the Cd L_3-edge to directly probe the Cd electronic structure of the particles. XMCD involves the use of circularly polarized x-rays as a probe of majority/minority spins in a sample and

Figure 2. Cd L_3-edge (a) XAS and (b) XMCD spectra for a 2.6 nm CdSe-TOPO QD. The blue line is a guide for the eye. The inset illustrates the mechanism of surface magnetism in CdSe QDs (π-backbonding from Cd atoms to empty π^* orbitals on the ligand)

provides element specific information of the orbital and spin angular momentum. Figure 2 illustrates that CdSe-TOPO QDs exhibit an XMCD signal at 3542 eV, an energy where vacant Cd d levels are expected to arise. The signal is on the order of $\sim 5 \times 10^{-4}$, which is consistent with a moment of $\sim 0.01 \mu_B$/Cd. Therefore, the correlation between the positive χ values, observation of an XMCD signal at the Cd L_3-edge, and the increase in the ligand π-acidity indicates that paramagnetism is arising from the molecular level interactions occurring between Cd atoms and the surface ligands (see inset Figure 2). Thus a series of magnetic measurements, including temperature dependent magnetization, isothermal magnetization, attempts to measure any remnant magnetization, and XMCD find no evidence for ordered magnetism in any of the measured CdSe QDs.

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